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The Role of Comprehensive Detailed Chemical Kinetic Reaction Mechanisms in Combustion Research

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Chemical Engineering Greetings to Professor Eliseo Ranzi on Occasion of his 65th Birthday

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THE ROLE OF COMPREHENSIVE DETAILED CHEMICAL KINETIC REACTION MECHANISMS IN COMBUSTION RESEARCH

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Recent developments by the authors in the field of comprehensive detailed chemical kinetic reaction mechanisms for hydrocarbon fuels are reviewed. Examples are given of how these mechanisms provide fundamental chemical insights into a range of combustion applications.

1. INTRODUCTION

Practical combustion consists primarily of chemical heat release from reactions between a fuel and an oxidizer, and computer simulations of practical combustion systems have become an essential tool of combustion research (Westbrook et al., 2005). At the heart of most combustion simulations, the chemical kinetic submodel frequently is the most detailed, complex and computationally costly part of a system model. Historically, the chemical submodel equations are solved using time-implicit numerical algorithms, due to the extreme stiffness of the coupled rate equations, with a computational cost that varies roughly with the cube of the number of chemical species in the model. While early mechanisms (c. 1980) for apparently simple fuels such as methane (Warnatz, 1980) or methanol (Westbrook and Dryer, 1979) included perhaps 25 species, current detailed mechanisms for much larger, more complex fuels such as hexadecane (Fournet et al., 2001; Ristori et al., 2001; Westbrook et al., 2008) or methyl ester methyl decanoate (Herbinet et al., 2008) have as many as 2000 or even 3000 species. Rapid growth in capabilities of modern computers has been an essential feature in this rapid growth in the size and complexity of chemical kinetic reaction mechanisms.

2. DETAILED KINETIC REACTION MECHANISMS

Detailed kinetic reaction mechanisms address combustion chemistry by providing the most complete description possible to include all chemical reactions and species that contribute to the observable reaction system. A conference organized by Gardiner and Edelson (1977) played a major role in the early days of detailed mechanisms. Detailed mechanisms make no concessions to the computational costs of the chemistry simulations, and often other portions of the combustion system model are simplified to accommodate the chemical kinetic submodel. As a result, detailed kinetic mechanisms are most commonly used in homogeneous reactor models of systems such as flow reactors, shock tubes, stirred reactors and rapid compression machines, and in systems that can be addressed in one-dimensional formulations such as premixed, laminar flames. Not surprisingly, these types of reactors have provided most of the information used to develop detailed kinetic

mechanisms (Westbrook and Dryer, 1984; Simmie, 2003). It is perhaps surprising to see how many important, essential features of many very practical combustion systems, including internal combustion engines, furnaces, industrial burners and others can be addressed using homogeneous or one-dimensional formulations, enabling detailed kinetic reaction mechanisms to play a significant role in practical research into the fundamentals of these systems, as discussed below.

3. COMPREHENSIVE CHEMICAL KINETIC MECHANISMS

Comprehensive detailed kinetic reaction mechanisms are a special type of detailed mechanism and occupy a somewhat more general position in combustion chemistry simulations. A detailed mechanism is intended to describe all of the important kinetic processes in a particular combustion environment, consisting of the specific ranges of pressure, temperature and fuel/oxidizer equivalence ratio in a given system. However, parameters that may be important in a high temperature shock tube experiment may not be the same as those in a low pressure laminar flame or in an intermediate temperature flow reactor simulation, so the detailed reaction mechanism for the shock tube simulation may be quite different from detailed mechanisms for other systems. A comprehensive mechanism is one that is valid under all possible conditions.

The concept of the "comprehensive" detailed kinetic mechanism was defined (Westbrook and Dryer, 1981) to describe a detailed mechanism that includes submechanisms for a wide range of operating parameters and can therefore be taken intact from one class of simulations to another without modification. In practice, the development of a comprehensive mechanism requires mechanism validation in every type of operating condition for which experimental results are available. For example, a recent comprehensive mechanism for n-heptane (Curran et al., 1998) developed a reaction mechanism that was validated by comparisons with data from shock tubes, flow reactors, stirred reactors, and rapid compression machines, and then subsequently in laminar flames and ignition in spark-ignition and diesel engines. A key feature of comprehensive reaction mechanisms is that they can be used with considerably greater confidence in new conditions than other detailed mechanisms. The most important feature of comprehensive mechanisms is their generality and the fact that multiple sets of experimental data have been used to test and refine them.

We have recently extended our previous comprehensive mechanism for n-heptane (Curran et al., 1998) to all of the n-alkanes from n-octane through n-hexadecane (Westbrook et al., 2008), shown in Figure 1. The mechanism for n-hexadecane included more than 2000 different chemical species, taxing computer resources of storage size and CPU speed currently available. In addition, the extensive validation studies of these mechanisms also show that the mechanisms are able to follow the details of combustion of these fuels over extended ranges of operating conditions.

However, a role of comprehensive reaction mechanisms that is perhaps not sufficiently appreciated is the ability to carry out "numerical experiments" to study features of hydocarbon oxidation that have not been examined previously. Two experimental shock tube studies (Ciezki et al., 1993; Pfahl et al., 1996) examined ignition of n-heptane and n-decane at elevated pressures over a range of temperatures from about 660K to 1260K. Computed values for the ignition delay times agreed well with the experiments for both fuels, as shown for stoichiometric cases at 13.6 bar pressure in Figure 2. The filled symbols in Fig.2 describe experimental and modeling ignition delay times for n-heptane and n-decane, and they show that not only does the model reproduce the experimental results very well, they also show that the ignition delay times for both n-alkanes are remarkably similar. In addition to intermediate temperature shock tube results, Fig. 2 also shows two other sets of computed and experimental results. At the highest temperatures, the shock tube experimental results of Zhukov et al. (2008) and accompanying model results, at the same pressure (13.6 bar) and equivalence ratio ($\phi = 1.0$) computed with the comprehensive mechanism for

- n-octane (n-C8H18)
- n-nonane (n-C9H20)
- n-decane (n-C10H22)
- n-undecane (n-C11H24)
- n-dodecane (n-C12H26)
- n-tridecane (n-C13H28)
- n-tetradecane (n-C14H30)
- n-pentadecane (n-C15H32)
- n-hexadecane (n-C16H34)

Figure 1. Schematic diagrams of n-alkanes from n-octane to n-hexadecane

n-decane are shown, and they show very clearly that they provide an extension of the lower temperature results of Pfahl et al. (1996) for n-decane. Even more interesting are the results in Fig. 2 at the lowest range of temperatures, showing results from a rapid compression machine study of Kumar et al. (2007) and computed results using our comprehensive mechanism for n-decane, also at approximately 13.6 bar pressure. It is important to note that the RCM data were produced from slightly lean (i.e., $\phi = 0.8$) mixtures and the delay times were scaled to stoichiometric conditions for Fig. 2. The RCM results evidently fit very continuously into the single ignition delay time curve based on the shock tube results. The curve is complicated by the existence of a region of negative

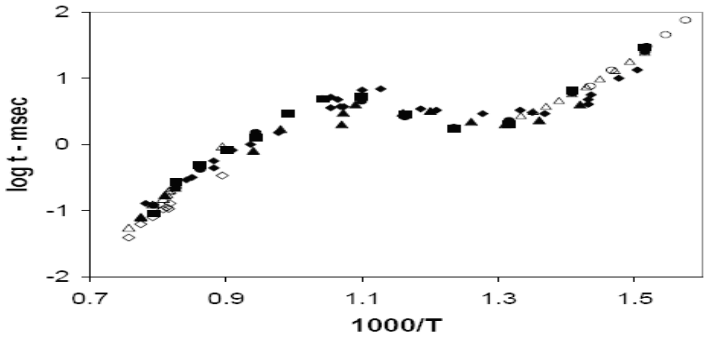

Figure 2. Ignition delay times for n-heptane and n-decane. Experiments are from Ciezki and Adomeit for n-heptane (♦) and Pfahl et al. for n-decane (▲). Computed values are shown for n-heptane (■) and n-decane (●). Open symbols at highest temperatures represent shock tube experiments (◊) of Zhukov et al. (2008) and model results (Δ) and open symbols at lowest temperatures show RCM results of experiments (Kumar et al., 2007) (Δ) and model calculations (○).

temperature coefficient (NTC) of ignition, but for these mixtures and experiments, it appears that ignition does not depend on the nature of the experimental facility being used to observe ignition.

There are clearly limits to this behavior, since it depends on the relative times of the RCM compression stroke and ignition delay time, but the same type of behavior has been reported for propane by Petersen et al. (2007). Calculations using the comprehensive reaction mechanism permit us to unify these ignition results, providing a very strong unifying analysis.

The similarities between ignition delay times for n-heptane and n-decane shown in Fig. 2 led us to examine the ignition of the other n-alkanes from n-heptane to n-hexadecane. Since no experiments have been carried out for any other n-alkanes besides n-heptane and n-decane, this comparison was carried out using the n-alkane kinetic mechanisms. All these calculations were carried out at 13.6 bar, with stoichiometric mixtures in air, and the results are summarized in Fig. 3. On this figure, it is impossible to distinguish one curve from another, and that may be the most important result of these calculations, and very similar results have been reported by Battin-Leclerc (2008). With closer examination, systematic differences between the different n-alkanes can be detected, and at an initial temperature of 900K in Fig. 3, the n-alkanes ignite according to their cetane numbers, with n-hexadecane the fastest to ignite and n-heptane the slowest, but all the ignition delay times are virtually identical over most of the range of temperatures shown in Fig. 3. These results have important implications about the role of kinetics in determining cetane ratings in Diesel engines, and these results are available only due to the existence of the comprehensive kinetic mechanism. These results also have significant implications concerning the choice of constituents in surrogate fuel mixtures for Diesel and gas turbine fuels.

A very similar result was found from experiments and modeling calculations for jet-stirred reactor oxidation of n-decane and n-hexadecane by Dagaut and Cathonnet (2006) and Ristori et al. (2001). Comparisons between computed chemical species concentrations and experimental results of Ristori et al. (2001) are shown in Fig. 4 for a specific set of operating parameters, and similar comparisons between experimental and

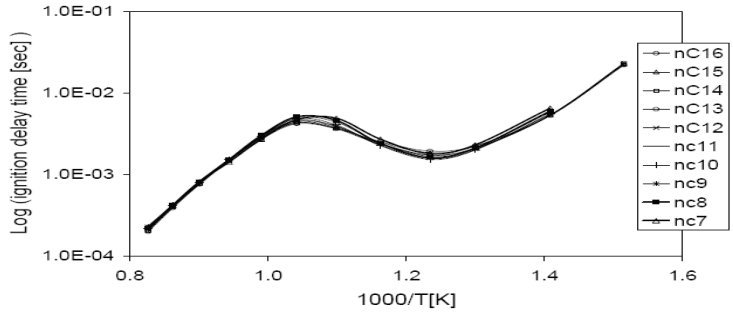

Figure 3. Computed ignition delay times for stoichiometric n-alkane/air mixtures from n-heptane through n-hexadecane. All results were at 13.6 bar.

computed results fueled by n-decane showed the same degree of agreement. The computed results are good enough to justify use of the comprehensive reaction mechanism to carry out another series of "numerical experiments" on n-alkane oxidation in the jet stirred reactor.

Numerical experiments were carried out under the same jet-stirred reactor conditions reported for 700 ppm n-decane by Dagaut et al. (1994, 2002), at atmospheric pressure, residence time of 0.07s, $\phi = 1.0$, for n-octane, n-decane, n-dodecane, n-tetradecane and n-hexadecane. Inlet concentrations for each n-alkane were scaled to match the carbon atom flux with that for n-decane; therefore the inlet levels were (n-octane/O_2) = (875 ppm/10938 ppm), for n-decane (700 ppm/10850 ppm), for n-dodecane (583 ppm/10750 ppm), for n-tetradecane (500 ppm/10750 ppm),

and for n- hexadecane (438 ppm/10718 ppm). While the fuel mole fraction curves are different in order to keep the carbon flux constant for all of the mixtures, a much different result is observed for nearly all of the other species in the group of calculations, as shown in Figure 5 in which the levels of ethene, methane and 1-butene are plotted. The computed concentrations of these species are very nearly equal to each other, regardless of the n-alkane fuel being used. It appears that any large n-alkane fuel could serve as a reliable surrogate for any of the others, as long as the fuel level is properly scaled. In this case, n-octane, n-dodecane, n-tetradecane and n-hexadecane all predict the same values for the major intermediates.

Another comprehensive kinetic mechanism has been developed for methyl cyclohexane by Silke et al. (2007), which is an example of a class of hydrocarbon fuels, cyclic paraffins, that must be considered when developing surrogate fuel mixtures for practical transportation fuels. Detailed models for cyclohexane (Sirjean et al., 2007; Pitz et al., 2007) and methyl cyclohexane (Silke et al., 2007) have provided important new information about the key reaction sequences in their oxidation. For example, at low and intermediate temperature conditions, alkylperoxy radical (RO_2)

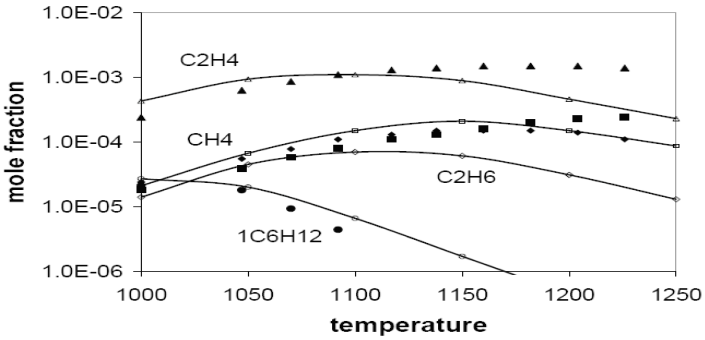

Figure 4. Comparison between computed and experimental (Ristori et al., 2001) results for selected species in n-$C_{16}H_{34}$ oxidation in a JSR. Conditions are $\phi = 1.5$, 1 atm pressure, and 0.07 s residence time.

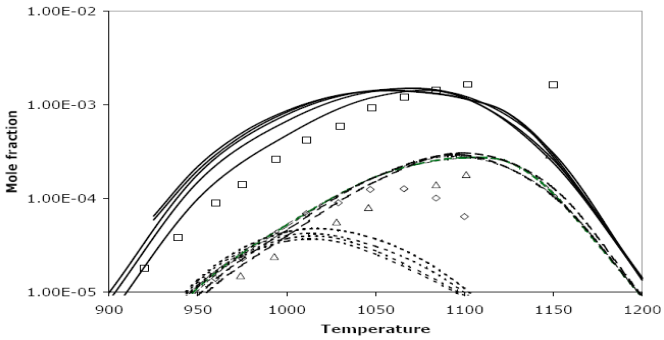

Fig. 5. Computed concentrations of ethene (solid lines), methane (dashed lines) and 1-butene (dotted lines) for n-alkane fuels under jet-stirred reactor conditions. Symbols represent experimental values from Dagaut et al. (1994, 2002) for n-decane oxidation, ethene (□), methane (◊), and 1-butene (Δ). Fuels included n-octane, n-decane, n-dodecane, n-tetradecane and n-hexadecane.

isomerization reactions are understood (Westbrook et al., 1991) to play a major role in autoignition and contribute to engine knock in spark-ignition engines. The rates of the RO_2 isomerization reactions in linear and branched alkane hydrocarbons have been shown to depend on the types of C-H bonds being broken and the sizes of the relevant transition state rings that participate in the isomerization reaction in predictable ways. However, when these rules for reaction rates were first applied to similar alkylperoxy isomerization reactions in cyclic paraffins, the predicted results showed serious errors when compared to experimental results. Subsequent kinetic analysis determined further dependences of these isomerization reactions that included the effects of the cyclic paraffin structures, and these structural effects unique to cyclic paraffins were important contributions from the comprehensive mechanisms for these fuels.

A very recent comprehensive kinetic mechanism was developed by Herbinet et al. (2008) for a large methyl ester species, methyl decanoate, shown schematically in Fig. 6.

Figure 6. Schematic diagram of methyl decanoate, a proposed biodiesel surrogate.

This species was selected as a potential surrogate to represent biodiesel fuel, which is the subject of considerable current attention due to increasing demands on petroleum-based fuels. Both soy methyl ester, the primary biodiesel candidate in the United States, and rapeseed methyl ester, the primary biodiesel candidate in Europe, consist of mixtures of only 5 major constituents, shown in Fig. 7, although the relative amounts of each constituent are different in the two biodiesel fuel mixtures. The similarities between methyl decanoate (Fig. 6) and the components of biodiesel fuel are clear, particularly if some double-bonded relatives of methyl decanoate could be included.

Herbinet et al. (2008) compared results for jet-stirred reactor experiments fueled by rapeseed oil methyl ester (Dagaut et al., 2007) and n-decane shock tube results (Davidson, 2001; Pfahl et al., 1996), with computed results using the methyl decanoate comprehensive mechanism, with excellent results. Comparison between experimental and computed results for jet-stirred reactor oxidation of rapeseed oil methyl ester (Dagaut et al., 2007), and computed results for a surrogate fuel with methyl decanoate and n-heptane are shown in Fig. 8. The n-heptane was added to the methyl decanoate to make the C/H ratio similar to that in the rapeseed methyl ester experiments. The methyl decanoate mechanism was used to simulate a series of shock tube

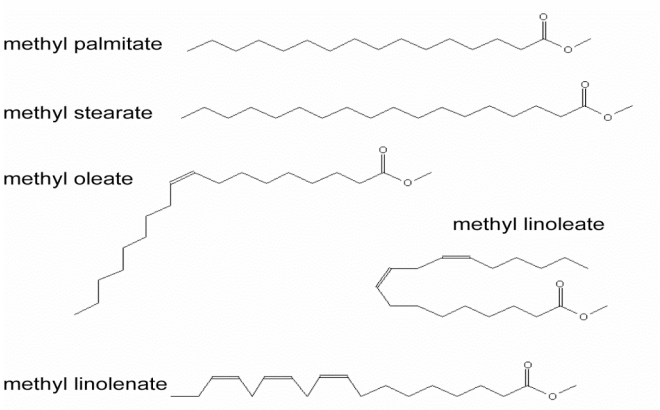

Figure 7. Major constituents in biodiesel fuels.

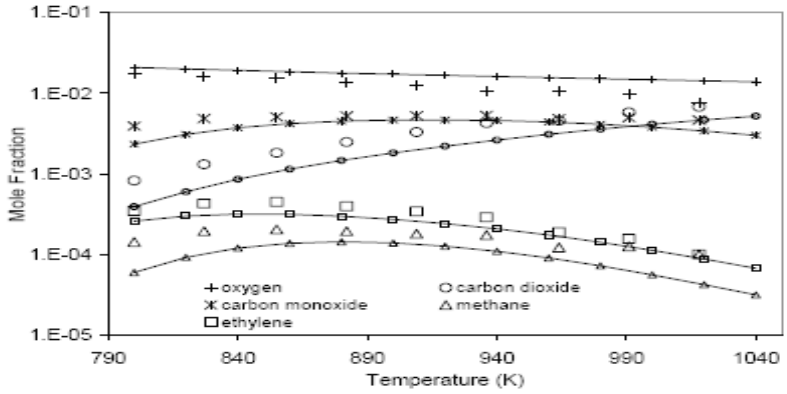

Figure 8. Comparison of jet stirred reactor oxidation of rapeseed oil methyl ester (P=10 atm, ϕ = 0.5, t_{res} = 1 s) (Dagaut et al., 2001) with computed results (Herbinet et al. 2008).

experiments of Davidson et al. (2001) and Pfahl et al. (1996) in which the fuel was n-decane. The agreement was excellent between the experimental values in the n-decane experiments and the results computed using the methyl decanoate mechanism, as shown in Fig. 9. Similarly, but not shown, the calculated and measured results for the intermediate temperature shock tube experiments of Pfahl et al. (1996) shown in Fig. 2 agreed very well. The good agreement was attributed to the fact that the length of the carbon atom chain in methyl decanoate is 10 C atoms, the same as the chain length in n-decane. The results discussed earlier and illustrated in Fig. 2 and 3 indicate that the results computed by the methyl decanoate mechanism would be expected to give good agreement with experiments carried out for any n-alkane between n-heptane and n-hexadecane. These results have important implications with regard to surrogate fuel composition for diesel and especially for biodiesel fuels in practical combustion systems. Addition of small methyl esters, such as methyl butanoate (Fisher et al., 2000; Gaïl et al., 2007) to n-decane or n-heptane have also been found to provide excellent agreement with rapeseed oil and soy oil biodiesel fuels in biodiesel simulations (Reitz, 2008).

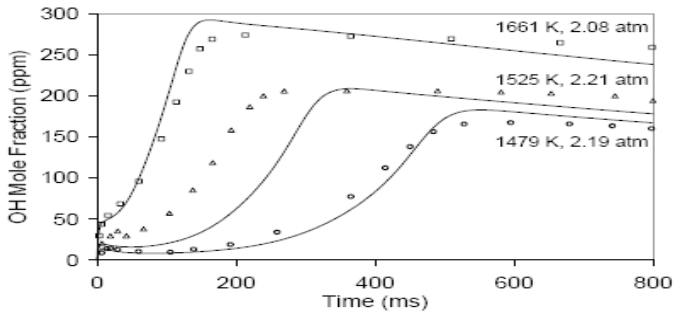

Figure 9. Computed OH mole fractions in n-decane ignition is shock tube experiments of Davidson et al. (2001).

4. MECHANISM REDUCTIONS

While detailed and comprehensive reaction mechanisms have the beneficial properties of great generality, they also involve significant computer costs in simulations of applied problems, and these costs lead to two major types of limitations. First, detailed mechanism calculations are time-consuming even when the kinetic model is the only important part of the simulation. One series of homogeneous medium calculations for the conditions shown above in Fig. 2 over the temperature range from 650K to 1200K required 8 hours of laptop computer time, so the turnaround time for results can be considerable. Time demands for one-dimensional laminar flame calculations with large reaction mechanisms can be even more time-consuming and inconvenient. When the modeling assignment requires a multidimensional treatment, detailed reaction mechanisms become prohibitively expensive.

A second drawback to full detailed reaction mechanisms is that the basic features of the combustion can sometimes be obscured by the great level of detail in the kinetics calculations. For example, when the fuel/oxidizer system exhibits a period of negative temperature coefficient (NTC) behavior, many parts of the detailed reaction mechanism show very similar kinetic details of $R + O_2 = RO_2$ and $QOOH + O_2 = O_2QOOH$ equilibrium, although the phenomenon is actually quite simple and can be reproduced in very satisfactory fashion with a much more simplified reaction mechanism.

Many techniques have been developed for simplification of detailed kinetic reaction mechanisms to provide a much more economical model. Most mechanistic reductions exploit the fact that many chemical species are effectively coupled together via rapid reactions between them, so changes in concentrations of one species can be used to predict the behavior of many others. As a result, many time-dependent coupled differential equations can be replaced by simple algebraic expressions that reduce the overall cost of the kinetic calculations. The mechanism reduction approach developed by Ranzi provides an interesting alternative method for mechanism reduction.

5. LUMPED MECHANISMS OF RANZI

Species lumping, as developed extensively by Ranzi and his collaborators (Ranzi et al., 1994,1995; Ranzi, 2006; Faravelli et al., 1998; Violi et al., 2002) and others has an advantage over other, more automated reduction techniques in the sense that they both can require and provide greater kinetic insights than many other techniques. In most of the above techniques, mechanism reduction occurs during the solution of the full set of coupled differential equations and is carried out within the solution software. Ongoing analysis of the time constants and Jacobians of the numerical model carry out the reductions and the results are usually transparent to the people carrying out the simulation.

In contrast, lumping techniques usually involve *a priori* identification of the species to be lumped together, most frequently depending on chemical insights based on experience with the detailed kinetic mechanism or to the intrinsic nature of the reacting system. This leads then to a specific simplification in the reaction mechanism which is enforced before simulations can proceed, and the results of that lumping process emerge directly from the computed results from the modified reaction mechanism.

An illustration of this type of lumping is the work of Held et al. (1997) and Chaos et al. (2007), for high temperature oxidation of n-alkane hydrocarbons, used for simulations of flames, shock tube ignition, and combustion in the turbulent flow reactor. In such systems, the n-alkane fuel is consumed by H atom abstraction to produce a number of structurally distinct alkyl radicals;

in the case of n-heptane there are 4 such structurally distinct heptyl radicals, which react via internal H atom transfer pathways to produce other heptyl radicals. By recognizing that the heptyl radicals inter-react rapidly and therefore produce a mixture of all of the heptyl radicals, production and subsequent decomposition of all these heptyl radicals can be lumped together into a single "overall" heptyl radical with a combination of decomposition reaction pathways that reconstruct the actual system behavior at a reduced computational cost and excellent accuracy.

A second example of the great value of the type of lumping developed by Ranzi is somewhat more complex than the alkyl radical lumping example above, but ultimately more important in the impact of the results. This example made a significant contribution to the development of comprehensive detailed kinetic reaction mechanisms for the gasoline primary reference fuels n-heptane and iso-octane (Curran et al., 1998, 2002), and the lumping contributions were carried out by Gaffuri, following his work as a graduate student of Professor Ranzi and employing his modeling techniques. To properly assess this contribution, it is necessary to describe briefly the overall structure of the reaction pathways that control low temperature hydrocarbon oxidation and the negative temperature coefficient of that reaction, as summarized graphically in Figure 10. Under high temperature conditions, alkyl radicals decompose thermally to produce smaller alkyl radicals and olefins, but at temperatures below about 800K, this decomposition pathway is very slow. Instead, under such conditions of lower temperatures and high pressures as commonly exist in spark-ignition and diesel engine ignition, alkyl radicals primarily react by adding to molecular oxygen to produce alkylperoxy radicals (RO_2). Since the reverse, decomposition route for these addition reactions has a relatively high activation energy, the adducts are relatively stable and have sufficient time to transfer H atoms within

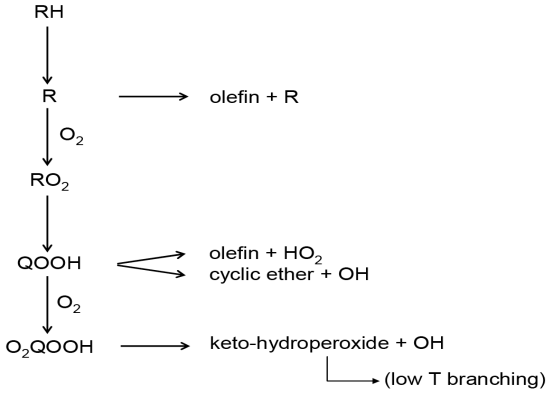

Figure 10. Schematic reaction flow diagram for hydrocarbons.

themselves to produce hydroperoxyalkyl radicals (QOOH) which are also relatively stable radical species. Therefore, these QOOH radicals can then add another oxygen molecule to produce O_2QOOH radicals that also persist for some time at these low temperatures. It is the fate and resulting impact of these O_2QOOH species that tell the interesting and important story.

O_2QOOH radicals transfer H atoms internally within that radical species, producing an intermediate species that is relatively unstable to decomposition to produce OH radicals. In preliminary versions of this mechanism development, it was first assumed that the product X of the decomposition reaction was also very unstable and

$$O_2QOOH \rightarrow OH + X$$

rapidly decomposed to smaller species. With this assumption, computed overall oxidation rates for both n-heptane and iso-octane were significantly overpredicted.

Gaffuri used the lumping techniques from Ranzi's group in Milano to address the same problem of low temperature oxidation of n-heptane and iso-octane. Because the lumped mechanism was more streamlined and the computed reaction fluxes in the results were easier to understand, it became clear that a critical step had been omitted from the detailed mechanism. The product species X in the above reaction of O_2QOOH was found to be a ketohydroperoxide intermediate with considerably greater stability that had been first assumed, and it resisted the immediate decomposition that had been predicted in the original detailed kinetic mechanism. This delays the onset of degenerate chain branching until the reacting mixture reacts at a somewhat higher temperature than in the previous calculations, with much better reproduction of experimental results.

These are important details that have big impacts on the timing of hydrocarbon ignition in internal combustion engines and their inclusion in detailed kinetic reaction mechanisms is essential for useful applications. Ignition timing is critical to the performance of Homogeneous Charge, Compression Ignition (HCCI) engines, to the onset of engine knock and Octane Number ratings of fuels in spark-ignition engines, and to ignition in diesel engines that controls the ratio of premixed to diffusion burning and NO_X production. This is an application in which the lumped model made a critical contributation to the development of the detailed mechanism. The detailed mechanism is necessary to explain the details of the variations in kinetics and ignition properties with the molecular structure of the fuel, and the detailed mechanism contributes information to improve the lumped mechanism, but the lumped mechanism made a key contribution to the detailed mechanism by identifying a missing portion of the overall reaction pathway that didn't depend on the specific molecular structure of the fuels.

This process of using lumped approaches to identify areas in a detailed kinetic mechanism that need improvements continues to the present. Another Ranzi graduate student, Dr. Marco Mehl, is currently working to refine the reaction pathways that consume olefin compounds that are produced during oxidation of n-alkanes but can also be primary fuels themselves. Earlier detailed kinetic mechanisms have emphasized combustion of alkane fuels, so approximate treatments of the intermediate olefin species were generally sufficient, but for more careful mechanisms and in situations where the fuel initially contains substantial levels of olefins, such an approximation in the olefin submechanisms is not satisfactory. Preliminary results for ignition delay times from comprehensive mechanisms for the three linear isomers of hexene (C_6H_{12}) are compared with experimental results of Vanhove et al. (2005) in Fig. 11.

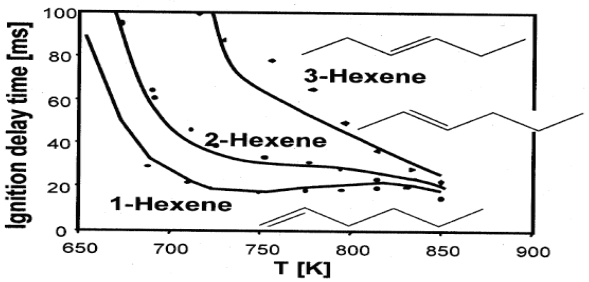

Figure 11. Computed ignition delay times for linear isomers of hexene from Mehl et al. (2008) compared to experimental values from Vanhove et al., (2005).

The isomers of hexene can be seen to exhibit varying amounts of NTC behavior, with the most NTC behavior in the case of 1-hexene, and the modeling shows that the longest un-interrupted chain of saturated -CH_2- groups in 1-hexene produces the largest amount of RO_2 isomerization and resulting NTC behavior. Again, the comprehensive reaction mechanism not only reproduces the observed results, but it also provides the kinetic insights to derive fundamental explanations for those results. Additional detail can be found in Mehl et al. (2008).

6. CONCLUSIONS

We have discussed a number of applications in which comprehensive reaction mechanisms provide unique computational tools for analysis of practical combustion systems. These comprehensive mechanisms illustrate recent advances in kinetic modeling capabilities, and we have highlighted several cases in which significant contributions were provided by lumped mechanism techniques pioneered by Eliseo Ranzi and his colleagues and students.

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